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INTERLABORATORY COMPARISON OF PASSIVE SAMPLERS FOR ORGANIC VAPOURS WITH RESPECT TO THEIR APPLICABILITY TO INDOOR AIR POLLUTION MONITORING: A PILOT STUDY

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INTERLABORATORY COMPARISON OF PASSIVE SAMPLERS FOR ORGANIC VAPOURS WITH RESPECT TO THEIR APPLICABILITY TO INDOOR AIR POLLUTION MONITORING: A PILOT STUDY

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ABSTRACT

This document reports on analytical work carried out in cooperation among three European laboratories. The purpose of this work was to carry out a first assessment on the performances of passive samplers for organic vapours when used in indoor air pollution monitoring and simultaneously to evaluate the interlaboratory agreement on low concentration analysis of a variety of volatile organic compounds.

Two types of passive samplers were thus exposed in the different facilities and replicate specimens were analysed at each of the three laboratories. The most important finding was that differences seem to exist between different specimens of the same sampler type. Overall reproducibility and accuracy has been within 40%, but reproducibility was better than 20% if a correction for the effect of systematic differences between samplers was introduced.

INTRODUCTION

In the framework of a European research collaboration in the field of Indoor Air Quality sponsored by the Commission of the EC and its Joint Research Center (JRC) the assessment of indoor pollution by organic gases and vapours has been identified as a priority objective. One important way to achieve this goal is the analysis of air samples collected in a possibly wide variety of indoor spaces.
Therefore a simple, inexpensive and not disturbing sampling method is required. Passive samplers are small inexpensive devices consisting of an active charcoal strip or disk and an envelope providing a diffusion gap; they have been developed for personal and space monitoring of volatile organic air pollutants in work place atmospheres and would meet these requirements. However, concentrations of organic air pollutants in non industrial indoor environments are typically 1-3 orders of magnitude lower than relevant concentrations in work place atmospheres. Therefore a problem of sensitivity arises.
We report here on pilot experiments performed jointly by the Hygiene Institute of the Aarhus University (HIA), the Institute for Water, Soil and Air Hygiene (WaBoLu) of the Federal Health Office, Berlin, and the JRC. This pilot study was intended to give a first information on the reproducibility, the accuracy and the sensitivity of passive sampler measurements, as well as on the range of compounds for which this sampling principle is suitable. Moreover, the study should give some information on the stability of loaded samplers when mailed over long distances. The question is of interest for large-scale measurement campaigns where different (geographically distant) laboratories would participate in the analysis of exposed samplers.

The results of these experiments are not supposed to provide a definite answer to the question whether or to which extent passive samplers might be reasonably applied to the measurement of volatile organic indoor air pollutants. The limited effort which could be invested in this pilot study was rather aimed at assessing whether a more detailed study is worthwhile and to which parameters or details it should pay particular attention.
Two laboratory experiments have been carried out: one set of samplers was exposed in a climate chamber of the HIA (Aarhus), another set at the WaBoLu (Berlin).

EXPOSURE (sampling) CONDITIONS

a. Aarhus experiment

Two types of passive samplers, the 3500 Organic Vapor Monitor (3 M Company) and the Gasbadge Organic Vapor Dosimeter (National Mine Service Company), were exposed for 23 hours, distributed over 4 days, in January 1983, to vapours of 15 organic compounds (see Table 1). During this time, air was also drawn through a charcoal tube (manufactured by the SKC Company following NIOSH recommendations). The type of compounds and the concentration values during exposure (of about 9.5 mg per m^3 of air, see below) reflect average conditions of new Danish dwellings.
The exposure took place in a climate chamber (83 m^3) at the HIA. Figure 1 shows schematically the exposure facilities, in which recirculation of air ensures perfect mixing of the added pollutants. The indoor climate conditions during exposure were 23°C and 45% RH.
The total compound concentration during exposure was monitored

by a FID detector calibrated with toluene, to keep it constant at the selected value (9.5 mg/m^3).

The pollutants were introduced into the ventilation system as fine droplets of the liquid mixture, which were evaporated by heating.

Nine samplers of each type were placed in the chamber, including three which were left sealed to act as blank controls. The air volume sampled through the charcoal tubes was accurately measured and ranged between 146.7 and 164.9 liters. The samplers were suspended to a horizontal string at the centre of the chamber 180 cm above the floor. The two types of passive samplers alternated with 15 cm separation. Traditional charcoal tubes were placed at the same height in the centre of the room.

Immediately after sampling the samplers (three of each type, including the blank) were sealed and mailed to the two other participating laboratories.

Table 1 - Composition of the liquid mixture of 15 compounds used for the exposure in Aarhus

Compounds	Concentration in liquid mg/g
n-Hexane	30.84
Cyclohexane	3.52
1-Octene	0.30
Ethylacetate	43.44
Isopropanol	3.49
3-Methyl-2-Butanole	3.69
n-Decane	34.07
4-Methyl-2-Pentanone	3.68
a-Pinene	39.42
Butylacetate	407.98
n-Hexanal	12.23
n-Butanol	40.41
1.3-Xylene	369.03
n-Propylbenzene	3.94
1.2.4-Trimethylbenzene	3.98

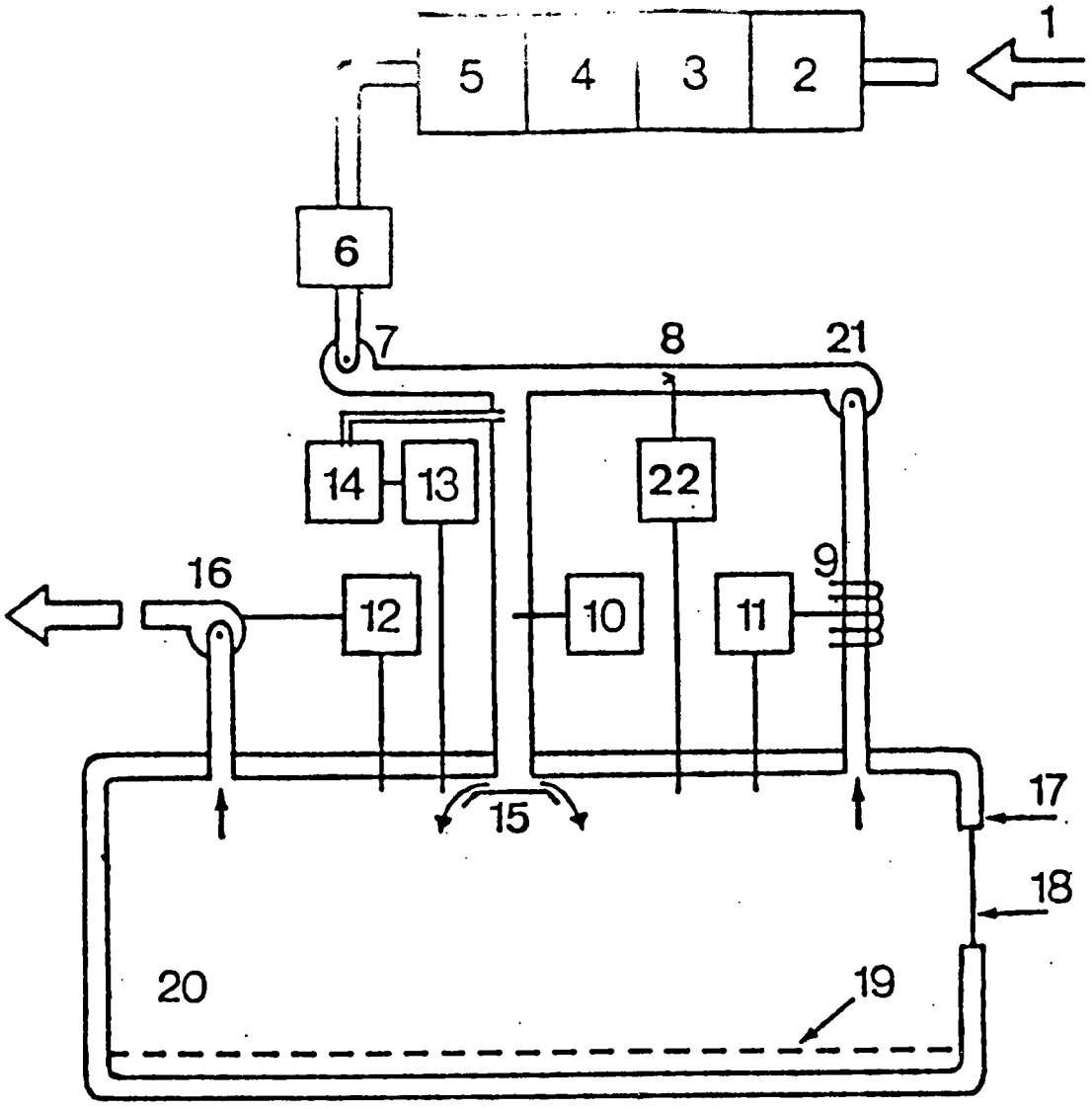

Fig. 1 - The climate chamber at the Institute of Hygiene, Aarhus, Denmark

1. Inlet of fresh air
2. Absolute particle filter
3. Active charcoal filter
4. Dehumidifier
5. Temperature control
6. Air volume measurements
7. Ventilator for ventilation air
8. Inlet of water vapours
9. Electric heating and for fine adjustment of temperature
10. Control for explosion danger
11. Control for air temperature
12. Control for air pressure
13. Total hydro-carbon-detector (FID detector)
14. Inlet of gases and vapours
15. Inlet slit, 5 mm x 6 m
16. Outlet ventilator
17. Stainless steel walls with insulation and heating circuits
18. Four layers of glass
19. Elevated, perforated floor
20. Chamber (volume 83 m^3)
21. Recirculation of room air
22. Humidity control

b. Berlin experiment

Six OVM-3500 samplers and six Gasbadge samplers have been exposed for two weeks in march 1983 in an all-glass exposure chamber of 1 m^3 (see Fig. 2). The chamber has been purged with a test gas mixture containing six components at known concentrations (see Table 2). The mixture was obtained by generating a concentrated primary gas mixture in a permeation device and diluting it with purified dry air. A flow of 290 l/h of the resulting test gas mixture has been maintained throughout the exposure period of 337 hours by means of a Brooks mass flow controller.

The concentrations of the six components in the test gas mixture- as determined by weighing the permeation tubes periodically - are reported in Table 2.

Table 2 - Concentrations of the test compounds during exposure

n-hexane	122 ± 3 $\mu g/m^3$
n-heptane	19.8 ± 4.0
benzene	34.9 ± 1.8
toluene	78.6 ± 1.4
1.3 xylene	18.2 ± 1.3
1.1.1-trichloro-ethane	12.0 ± 2.7

Three Gasbadge samplers were equipped with additional filter elements for blank analysis.

ANALYTICAL TECHNIQUES

a. Hygiene Institute, University of Aarhus

The passive samplers were eluted following the recommendations given by the respective manufacturers*, except for using as solvent N.N.-dimethylformamide instead of carbon disulfide. The charcoal tubes were eluted with the same solvent, for 24 hours at 27°C, using 2 ml for each section of the tube. All eluates as well as blanks and standards were analysed by gas-chromatography, employing a HP-5720 instrument with a 100 m x 0,25 mm capillary column coated with CW20 M; the carrier gas was helium at 2 cm^3/min and the volume injected 1 μl with 1:10 splitting. Any other detail of the analytical technique may be found in Ref. (1).

The analyses were carried out several months after exposure of the samplers, when another set of samplers exposed in the field had to be analysed; in the meantime the samplers were stored in refrigerator at - 40°C. The reference solution contained only 10 out of the 15 compounds adsorbed on the samplers: this is the reason why no results are available for 1-octene, ethylacetate, n-decane, a-pinene and n-hexanal.

No replicate analyses could be performed due to lack of time and, finally, this was the first occasion in which passive samplers were dealt with in Aarhus.

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* see annex 1 and 2.

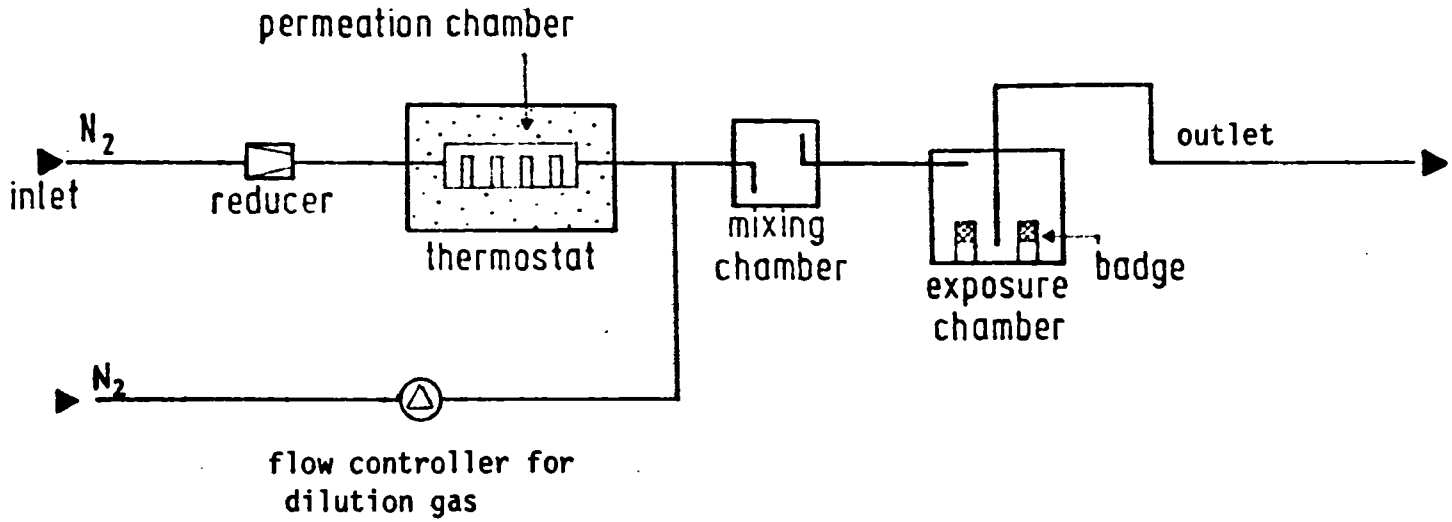

Fig. 2 - The exposure chamber at the Water, Soil and Air Hygiene, BERLIN

b. Institute for Water, Soil and Air Hygiene, Berlin

The active carbon pads of the passive samplers, as well as the combined content of the two active carbon sections of the NIOSH tubes, were extracted with CS_2. Prior to this extraction, 200 μg of cyclooctane in CS_2 was added to the active carbon as internal standard. 0.5 μl of the elution solutions were injected onto a gaschromatograph with an OV 1701 capillary column in the splitless mode.

Due to lack of reference compounds, 1-octene and 3-methyl-2-butanol could not be measured. Butylacetate and n-hexanal, as well as isopropanol and CS_2 could not be separated by the OV 1701 column. N-propylbenzene and n-decane were not well resolved on this column too. Whereas toluene was not mentioned to be part of the mixture of the Aarhus exposure experiment, all the samplers contained this compound as indicated in Tables 4 to 6.

c. Joint Research Centre, Ispra

The passive samplers were extracted with 2 ml CS_2, the charcoal tubes with 1,5 ml and analysed by GC via splitless injection, on an OV-1 column. A GC-MS run was also carried out to confirm identification of the different compounds.

Of the 15 compounds listed in Table 1, 3 are not reported, namely: 1-octene, because too low in concentration, isopropanol, because covered by the solvent peak and 3- methyl-2-butanol, because the reference compound was not available. On the other hand, toluene, not included in Table 1, was detected in all samplers and the observed amounts are given.

The calibration of the GC system for a-pinene and 1.2.4 trimethylbenzene was performed respectively with decane and m-xylene, due to lack of the former compounds.

Hexane and ethyl acetate which were not separated under our standard temperature conditions were separated at subambient temperature on the elution solution of one of the charcoal tubes and the proportion of the counts observed was applied to the merged peaks in all other samples, to derive the concentrations of the single compounds.

The analyses were carried out about two months after exposure due to travel and customs delay.

RESULT AND DISCUSSION

The chemical analysis gives the amount A of pollutant(s) extracted from a sampler. This value is converted into the mean air concentration c of the pollutant during the exposure period by means of the following equation:

$$C = A/(r \cdot V) \qquad (1)$$

where r is the recovery coefficient (or the fraction of the adsorbed pollutant which has been extracted)

and V - the sampled air volume in the case of active samplers
- a calibration factor in case of passive sampler which is experimentally determined and/or theoretically derived from the diffusion equation.

For passive samplers V is in general expressed as product of the sampling period t and an equivalent sampling rate S which is specific for each compound. For OVM 3500 samplers S cm^3/min values are supplied for most compounds of interest in industrial hygiene. For the GASBADGE TM samplers a calibration factor is given which has to be multiplied by the diffusion coefficient D[cm^2/sec]of a compound in order to obtain its sampling rate S.
With the two approaches concentration values are calculated using the following formulae:

$$C[\mu g/m^3] = 10^6\ A/(r.S.t) \quad \text{for the OVM 3500} \qquad (2)$$

$$C[\mu g/m^3] = 2{,}5.10^3\ A/(r.D.t) \quad \text{for the GASBADGE} \qquad (3)$$

sampler, where A is in μg/sampler and t in minutes.
Table 3 reports for the compounds used in the two exposure experiments available S and D values.
Measured A/r values and calculated concentrations are reported separately for the two exposure experiments.

The recovery coefficients r have been obtained in the following ways by the three laboratories:

- At HIA (Aarhus) the recovery correction was implicitly incorporated into the A values through addition of the absorbant (charcoal) to the reference solutions; thus the fraction retained was not measured both in the sample and in the standard.
- At the WaBoLu (Berlin), since no experimental results were available for the recovery of polar compounds, the recovery coefficient for all compounds analysed by passive samplers was set to 0.87, a mean value obtained for hydrocarbons (2). For active

samplers, a recovery coefficient of 1 was used: in the case of polar compounds, the same reason as for passive samplers applies, whereas for hydrocarbons, the recovery was experimentally found to be very close to 1.

- At the JRC (Ispra), a correction was introduced for only two compounds (butanol and hexanal), on the basis of some extraction efficiency tests performed in the laboratory. These tests showed no significant deviations of r from 1 for the other compounds tested, whereas for butanol and hexanal important losses occurred (r = 0.28 and 0.67 for butanol on resp. OVM-3000 and Gasbadge; r = 0.79 for hexanal on OVM-3500).

a. Aarhus experiment

The measured A/r values are reported in Tables 4 - 6, separately for the three sampler types. The Tables contain for each of the test compounds the mean and the difference of the two quantities determined for each couple of samplers.

In addition, the means of all A/r values obtained from a single sampler type and the associated relative standard deviations are given.

As already mentioned in the experimental section, a number of constituents have not been detected or quantified at all or not in all samplers due to one or several of the following reasons:

- too low concentration (1-octene)
- unavailability of reference compounds (ethylacetate, n-decane, α - pinene and hexanal at Aarhus, 3-methyl-2-butanole at Berlin, 3-methyl-2-butanole and α-pinene at Ispra)
- interference from the CS_2 (solvent) peak (isopropanol at Berlin and Ispra and to a lesser extent, ethylacetate and cyclohexane at Berlin) or

Table 3 - Sampling constants of passive samplers

	OVM-3500 S [cm^3/min]	GASBADGE D [cm^2/sec]
1.1.1-trichloroethane	30.9	0.0794
n-hexane	32.0	0.0732
n-heptane	28.9	0.0664 6)
n-decane	22.8 1)	
cyclohexane	32.4	0.0794 7)
a-pinene	23.5 2)	0.0630 8)
benzene	35.5	0.0932
toluene	31.4	0.0849
1.3-xylene + 1.4-xylene	27.3	0.0679
n-propylbenzene	24.0 3)	0.0669
1.2.4-trimethylbenzene	24.0 4)	0.0669
isopropanol	39.4	0.1013
butanol	34.3	0.0861
ethylacetate	34.5	0.0861
butylacetate	31.6	0.0672
3-methyl-2- butanole	33 5)	0.0793 9)
4-methyl-2-pentanone	30.0	

1) extrapolated from n-hexane to n-nonane values
2) estimated from values for n-nonane, n-decane and naphtalene
3) estimated from cumene
4) estimated from other alkylbenzenes
5) interpolated between 2-butanone and 4-methyl-2-pentanone
6) interpolated between n-hexane and n-octane
7) estimated from other hydrocarbon values
8) value of 1.4-cymene
9) value of methyl-propyl-ketone

Table 4 - Results obtained on the OVM-3500 samplers exposed in Aarhus

	HIA [µg/sampler]		WaBoLu [µg/sampler]		JRC [µg/sampler]		Overall mean	Standard dev.
	mean [1]	differ.	mean [1]	differ.	mean [1]	differ.	[µg/sampler]	[%]
n-hexane	11.0	5.2	8.9	(4)	17.2	4.6	12.4	28
cyclohexane	1.4	(4)	3.1	1.2	1.53	0.46	2.01	47
ethylacetate	-	-	14.9	(4)	19.2	5.1	17.0	19
isopropanol	1.4 (2)	-	-	-	-	-	-	-
3-methyl-2-butanol	1.4	(4)	(3)	-	-	-	-	-
n-decane	6.9	2.5	8.9	0.3	11.1	3.7	8.95	27
4-methyl-2-pentanone	-	-	(3)	-	0.69	0.26	-	-
a-pinene	-	-	11.3	0.8	11.9	2.6	11.6	10
butylacetate	139	66	126	1.5	126	36	130	19
n-hexanal	-	-			1.0	0.27	-	-
n-butanol	13.8	5.1	13.7	0.9	13.3	0.9	13.6	12
1.3-xylene + 1.4-xylene	111	63	134	1.6	147	44	131	22
n-propylbenzene	4.1 (2)	-	1.35	0.3	1.29	0.38	1.88	67
1.2.4-trimethylbenzene	-	-	1.95	0.9	1.89	0.78	1.92	25
toluene	13.7	7.8	14.0	0.4	15.6	4.6	14.4	21

(1) of the two samplers
(2) one value only
(3) both results below detection limit (1.3 µg)
(4) below detection limit

Table 5 - Results obtained on the GASBADGE samplers exposed in Aarhus

	HIA [µg/sampler]		WaBoLu [µg/sampler]		JRC [µg/sampler]		Overall mean	Stand. dev.
	mean [1]	difference	mean [1]	difference	mean [1]	differ.	[µg/sampler]	[%]
n-hexane	12.1	1.8	21.6	14.4	27.9	3.4	20.5	42
cyclohexane	1.9	(4)	6.25	4.3	2.86	0.16	3.67	67
ethylacetate	-	-	20.5	1.0	30.2	3.6	25.4	23
3-methyl-2-butanol	4.7	1.9	-	-	-	-	-	-
n-decane	10.3	1.9	10.3	0.6	10.5	0.3	10.3	6.2
4-methyl-2-pentanone	1.9	(4)	1.9	0.1	2.1	0.1	1.93	5.3
a-pinene	-	-	13.2	2.8	10.5	0.5	11.8	17
butylacetate	161	9	163	12	140	5	151	9.5
n-hexanal	-	-			-	-	-	-
n-butanol	8.5	1.7	0.8(2)	-	16.3	2.4	10.1	66
1.3-xylene + 1.4-xylene	147	11	184	34	160	4	163	13
n-propyl benzene	3.7	(4)	1.5	0.2	1.4	0.8	2.2	53
1.2.4 trimethylbenzene	16.8 (3)	-	2.2	0.3	2.1	0.06	5.0	132
toluene	23.3	1.8	24.9	8.2	19.3	0.3	22.5	17

(1) of the two samplers
(2) one value only; the other is below detection
(3) one value only
(4) below detection limit

Table 6 - Results obtained on the charcoal tubes exposed in Aarhus

	H I A [µg/sampler]		WaBoLu [µg/sampler]		JRC [µg/sampler]		Overall mean	Standard dev.
	mean [1]	differ.	mean [1]	differ.	mean [1]	differ.	[µg/sampler]	[%]
n-hexane	66.6	4.3	59.6	27.2	105	86	77.1	47
cyclohexane	10.2	1.7	13.7	5.2	8.46	2.95	10.8	29
ethylacetate	-	-	59.8	23.9	114	93	86.6	58
isopropanol	3.7	(3)	-	-	-	-	-	-
3-methyl-2-butanol	9.3	0.1	-	-	-	-	-	-
n-decane	54.6	9.7	63.8	52.9	67.6	27.2	62.0	32
4-methyl-2-pentanone	5.6	0.1	(2)		7.4	4.1	6.48	31
a-pinene	-	-	64.4	23.3	74.2	28.8	69.3	23
butylacetate	1066	177	702	289	678	276	815	29
hexanal	-	-						
n-butanol	88.8	15.5	40.5	20.3	31.3	9.4	53.5	54
1.3-xylene + 1.4 xylene	740	117	816	400	762	313	773	22
n-propylbenzene	13.0	3.9	8.0	4.1	10.5	4.7	10.5	31
1.2.4 trimethylbenzene	7.4	(3)	10.1	4.2	10.6	4.9	9.26	27
toluene	73.9	0.6	64.6	35.9	57.3	22.0	65.3	23

(1) of the two samplers
(2) both results below detection limit (1.3 µg)
(3) below detection limit

- insufficient GC separation (butylacetate/hexanal and decane/n-propylbenzene at Berlin, hexane/ethylacetate at Ispra. In this latter case separation was achieved for one sample using subambient temperature: the peak area ratio determined in this experiment has been used to correct the other values).

At Ispra the GC-response factor of n-decane has been used for α-pinene, which may result in an underestimate ($\leqslant 20\%$) of the α-pinene quantities.

Using values of S and D reported in Table 3 and equations (1), (2) and (3), the A/r values reported in Tables 4-6 have been converted to concentration values where possible (see Table 7). Besides the values obtained in each laboratory with each sampler type, mean concentration values obtained with the three sampler types and the overall mean concentrations and their relative standard deviations are given.

The results of the analysis of blank samplers are summarized in Table 8. At Berlin, blanks have not been analyzed together with the exposed samplers. Only later, five unexposed charcoal tubes of the same batch as those used during the exposure experiment have been analyzed.

For the discussion of the results it is important to note that the participating laboratories could only make a limited effort in these investigations because the scope of the experiment was not an in-depth study, but a rough assessment of the potential usefulness of passive samplers for non-industrial indoor air analysis, i.e. at concentrations in the $\mu g/m^3$ instead of the mg/m^3 range.

Hence, the following evaluation of reproducibility, accuracy and

sensitivty is intended to give indications rather than to arrive at stringent conclusions.

Reproducibility. For each couple of samplers the expression

$$R\ [\%] = \frac{1}{n} \sum_{i} \frac{|A'_{i1} - A'_{i2}|}{A'_{i1} + A'_{i2}} \cdot 200 \qquad (4)$$

has been calculated where A'_{i1} and A'_{i2} are the quantities of compounds i divided by the recovery coefficient r measured with the two samplers of each couple and n is the number of compounds which have been quantitatively detected. The values of R are reported in Table 9. The reproducibility of the duplicate analyses varies between 6 and 45%.

R varies considerably for the same sampler type and for the same laboratory. High R values are unlikely to be only caused by the analytical procedure (extraction+GC analysis) but are presumably due to variations of the sampler characteristics.

This becomes evident if the ratios A'_{i1}/A'_{i2} are calculated instead of the differences $A'_{i1} - A'_{i2}$. Table 10 shows the mean ratios

$$RA = \frac{1}{n} \sum A'_{i1}/A'_{i2} \qquad (5)$$

and their standard deviations for each couple of samplers analysed in either of the three laboratories. The mean ratios obtained with the OVM-3500 samplers at Aarhus and at Ispra and with the charcoal tubes at Berlin and at Ispra show considerable deviations from unity, exceeding the variability associated with the analytical procedure. Table 9 has therefore been recalculated introducing the following correction:

Table 7 - Comparison of air concentrations [1] measured through different samplers in the Aarhus experiment [$\mu g/m^3$]

Compound	Overall mean concent.	rel. SD %	mean concentrations			Results by HIA			Results by WaBoLu			Results by JRC		
			OVM3500	GASB.	CHARC. TUBE	OVM3500	GASB.	CHARC. TUBE	OVM3500	GASB.	CHARC. TUBE	OVM3500	GASB.	CHARC. TUBE
n-hexane	425	41	277	503	496	246	296	425	199	529	382	385	683	681
cyclohexane	57	38	45	-	69	31	-	65	69	-	88	34	-	55
ethylacetate	482	34	347	528	562	-	-	-	310	427	384	399	629	740
isopropanol	-	-	-	-	-	25	-	24	-	-	-	-	-	-
3-methyl-2-butanol	-	-	-	-	-	30	106	59	-	-	-	-	-	-
n-decane	340	24	282	-	399	217	-	348	280	-	409	349	-	439
4-methyl-2-pentanone	-	-	-	-	-	-	-	36	-	-	-	16	-	48
a-pinene	380	16	354	337	448	-	-	-	345	375	413	363	299	482
butylacetate	4104	30	2957	4123	5233	3150	4290	6800	2860	4350	4500	2860	3730	4400
n-butanol	317	36	284	258	388	289	177	566	286	17*	260	278	339	338
1.3-xylene + 1.4-xylene	4240	18	3433	4320	4967	2920	3880	4720	3520	4860	5230	3860	4220	4950
n-propilbenzene	64	48	67	59	67	122	99	83	40	40	51	39	38	68
1.2.4-trimethylbenzene	59	12	57	58	60	-	450*	47	58	59	65	56	56	69

(1) obtained from the data in Tables 4 - 6. using the data in Table 3 and the equations (1 - (3

* values not included in the calculation of the mean

Table 8 - Blank values observed in the different samplers [μg/sampler] [these data were obtained at the JRC, except those with notes 1) + 2)]

	OVM-3500	GASBADGE	CHARCOAL TUBE		
			A+	B+	2)
n-hexane	< 0.2	<1.8 - 3.8 [1)]	~0.2	~0.3	< 0.3
cyclohexane	< 0.2	<0.2	< 0.2	< 0.2	< 0.3-0.6
ethylacetate	< 0.3	2.0	< 0.3	< 0.3	< 0.3
n-decane	< 0.2	0.66	~0.2	~0.3	< 0.3-2.8
4-methyl-2-pentanone	<0.4	<0.4	< 0.4	< 0.4	< 0.3
a-pinene	<0.2	<0.2	< 0.2	< 0.2	< 0.3
butyl-acetate	<0.4	<0.4 - 7.5 [1)]	< 0.3	< 0.3	< 0.3
hexanal	*	*	*	*	
butanol	< 0.6	<0.6 - 13.2 [1)]	< 0.5	< 0.5	< 0.3
m-xylene	< 0.2 - 1.3 [1)]	0.54	0.63	< 0.2	< 0.3-2.0
n-propylbenzene	< 0.2	<0.2	< 0.2	< 0.2	< 0.3
1.2.4 - trimethylbenzene	< 0.2	<0.2 - (124) [1)]	< 0.2	< 0.2	< 0.3
Toluene	< 0.2	<1.1	< 0.2	< 0.2	< 0.3
Overall range	<0.2 - 1.3	<0.2 - 13.2	< 0.2 - 2.8		

1) values obtianed at the HIA-Aarhus
2) values obtained at WaBoLu, Berlin on five tubes
* not detected (see text)
\+ first and second section of the charcoal in the tube

$$RC\,[\%] = \frac{1}{n} \sum_{i} \frac{|A'_{i1}/RA - A'_{i2}|}{A'_{i1}/RA + A'_{i2}} \cdot 200 \qquad (6)$$

with RA values taken from Table 10. The corrected reproducibility values RC are reported in Table 11. They are consistently lower than the values of Table 9 and more likely in the range of the presumable analytical reproducibility.

In the case of the values obtained at Ispra this has been confirmed by repetitive GC-analysis of several sampler extracts. The relative standard deviations of the repetitively determined test compound quantities varied from 5 to 15% in good agreement with the figures of Table 11 obtained at Ispra. Comparing Tables 9, 10 and 11 it appears, that charcoal tubes show the strongest variations of the sampling characteristics, the OVM-3500 samplers vary to a lesser extent and that the GASBADGE samplers are the most homogeneous of the three sampler types. Since only a small number of each type of sampler has been analysed these results can only be an indication that the homogeneity of samplers needs further investigation.
Table 11 indicates that, apart from systematic differences between samplers, all sampler types and laboratories perform comparably well with respect to the reproducibility of the analytical result.

Accuracy. The accuracy of the results obtained with the different samplers could not be directly determined since the true concentrations of the individual test compounds during exposure are not exactly known.
Instead the overall mean concentrations shown in Table 7 are taken as an estimate of the true concentration values.
This assumption is supported by a comparison of the resulting

Table 9 - Reproducibility R of duplicate analyses

	OVM-3500		GASBADGE		CHARCOAL TUBE		$\bar{R}$
	R (%)	± SD	R (%)	± SD	R (%)*	± SD	
Aarhus	35	23	12	13	11	10	19
Berlin	12	17	24	23	37	13	24
Ispra	28	8	6	4	45	17	26
$\bar{R}$	24		14		31		

Table 10 - Mean ratios RA of test compound quantities extracted from each couple of samplers

	OVM-3500		GASBADGE		CHARCOAL TUBE		$\overline{RA}$
	RA	± SD	RA	± SD	RA*	± SD	
Aarhus	1,46	0,32	1,06	0,20	1,09	0,16	1.20
Berlin	0,99	0,22	1,27	0,41	1,48	0,24	1.25
Ispra	1,27	0,20	1,03	0,08	1,63	0,34	1.31
$\overline{RA}$	1,24		1,11		1,40	0,28	

Table 11 - Reproducibility of duplicate analyses after correction for sampler differences

	OVM-3500		GASBADGE		CHARCOAL TUBE		$\overline{RC}$
	RC (%)	± SD	RC (%)	± SD	RC (%)*	± SD	
Aarhus	17	15	13	10	10	7	13
Berlin	12	16	23	16	10	10	15
Ispra	12	16	5	4	15	10	11
$\overline{RC}$	14		14		12		

* corrected for differences of measured sample volumes

Table 12 - Overall mean and relative concentrations of test compounds and comparison of their respective (relative) standard deviations

	overall mean concentration [µg / m³]	rel. stand. deviation (%)	rel.overall mean conc. (%) 1)	rel.conc. in liq. test mixture 1)	% deviation $\frac{III-IV}{IV} \cdot 100$
	I	II	III	IV	V
n-Hexane	425	41	10.02	8.36	20
cyclo-Hexane	57	38	1.34	0.95	41
Ethylacetate	482	34	11.37	11.77	3
n-Decane	340	24	8.02	9.23	13
a-Pinene	380	16	8.96	10.68	16
Butylacetate	4.104	30	96.79	110.55	12
n-Butanol	317	36	7.48	10.95	32
m,p-Xylene	4.240	18	100.00	100.00	-
n-Propylbenzene	64	48	1.51	1.07	41
1,2.4-Trimethylbenzene	59	12	1.39	1.08	29

1) expressed as percent of the 1.3-1.4-Xylene concentration

Table 13 - Estimates AC of the accuracy obtained with the different samplers in the three participating laboratories

	OVM-3500		GASBADGE		CHARCOAL TUBE		AC (%) of LAB. MEANS
	AC (%)	± SD	AC (%)	± SD	AC (%)	± SD	
Aarhus	40	26	28	22	28	29	21
Berlin	23	16	12	15	20	13	14
Ispra	17	14	22	21	25	20	14
AC of sampler type means	17		9		16		

relative concentrations (in % of the xylene concentration, xylene being supposed not to present particular difficulties with respect to ad-and desorption) and the corresponding relative concentrations in the test mixture used for spiking the exposure chamber air, as shown in Table 12. The Table, besides giving the overall mean concentrations and their relative standard deviations (columns I and II), contains these two relative concentrations (columns III and IV) and their relative deviations (column V). With the exception of cyclohexane and 1, 2, 4-trimethylbenzene, the latter values are all within the relative standard deviations of the measured overall mean concentrations. Therefore the relative standard deviations of the overall mean concentrations may be considered as a good estimate of the accuracy of these experimentally determined concentrations, unless a systematic error affects the determination of all test compound quantities by the same factor, irrespective of the compound nature. In view of the diversity of the test compounds, such a hypothesis appears, however, rather unlikely.

The accuracy of the results obtained with the different samplers and in the different laboratories has been estimated comparing the relative standard deviations of the mean concentrations measured with each couple of samplers with the overall mean concentrations, using the equation

$$AC\ [\%] = \frac{1}{n} \cdot \sum_{i}^{1..n} \frac{|\bar{C}_i - \hat{C}_i|}{\hat{C}_i} \cdot 100 \qquad (7)$$

where $\bar{C}_i$ is the mean concentration of compound i determined with one couple of samplers, $\hat{C}_i$ is the overall mean concentration of the same compound and n is the number of compounds for which

both values have been determined. Results are reported in Table 13. The table contains also the average deviations of the mean concentration values obtained with each sampler type and in each of the laboratories from the overall mean concentrations.

Analysing Tables 12 and 13 it appears that the accuracy of concentration measurements is of the order of about 40% or better. Among the samplers the GASBADGE appears to perform best whereas differences between laboratories are less pronounced.

Detection limits. No particular attention has been payed to the evaluation of detection limits. Therefore out of the four factors which determine the minimum detectable amount of a substance (the solvent dilution factor, the extraction efficiency, the blank value of the sampler, and the sensitivity of the GC-analysis) only the blank values will be briefly considered. From Table 8 it results that, for the test compounds used in this experiment, blank values ranging from < 0.2 up to 13 μg have been determined. Assuming a signal/noise ratio of 3:1 as condition for unambiguous detection, detection limits ranging from 0.6 up to 40 μg/sampler derive, with typical values around 1-5 μg/sampler. This would be equivalent to 25-120 $\mu g/m^3$ for a 24 h exposure and to 4-17 $\mu g/m^3$ for a one week exposure.

b. Berlin experiment

The Berlin experiment has been designed for a comparison of true (expected) and measured concentration values. Therefore test compounds were released from thermostatted permeation tubes and diluted in a controlled flow of purified dry air. Thus, concentrations in the exposure chamber could be calculated from the weight loss of the permeation tubes and the dilution factor. The choice of the test compounds was determined by the availability

of appropriate permeation tubes.

In addition, the determination of test compound concentrations, via weight loss of the permeation tube has been checked by a well established sampling and analysis procedure using TENAX adsorption tubes, thermal elution of test compounds and GC analysis.
Concentrations determined by both methods are reported in Table 14 together with the mean values and the relative deviations from the mean in percent.
The relative deviations are all below 10%. It is therefore supposed that the mean expected concentrations correspond to the true concentrations within an accuracy of 10%.

The experimental results are summarized in Tables 15 and 16 separately for the OVM-3500 and the GASBADGE samplers. The tables report the mean and the difference of the two concentration values determined in each of the three laboratories using eqs. (2) and (3) and the S-respectively D-values reported in Table 3. In addition the overall mean concentrations per sampler type and their relative standard deviations are given.

In the following, the reproducibility and the accuracy of the measurements are discussed.

Reproducibility. In analogy to the evaluation of the Aarhus experiment, the reproducibility has been assessed by means of eqs. (4) and (5) substituting however the sampled amounts A by the measured concentrations c_i. The resulting values of R and RA are reported in Table 17.

Table 14 - Expected concentrations [$\mu g/m^3$] of test compounds in the Berlin exposure chamber

	expected concentrations determined by		mean expected concentration	Standard deviation
	weight loss	Tenax sampling	C	%
n-hexane	122	113	117.5	5.4
benzene	34.9	34.8	34.9	0.2
n-heptane	19.8	19.2	19.5	2.2
toluene	78.6	66.6	72.6	11.7
1.3 + 1.4-xylene	18.2	16.8	17.5	5.7
1.1.1.-trichloroethane	12.0	14.2	13.1	11.9

Table 15 - Test compound concentrations determined with OVM-3500 samplers exposed at Berlin

Compound	HIA mean* µg/m³	HIA difference* µg/m³	WaBoLu mean* µg/m³	WaBoLu difference* µg/m³	JRC mean* µg/m³	JRC difference* µg/m³	Mean conc. OVM 3500 µg/m³	relative SD [%]
n-hexane	61.2	29.7	84.7	14.1	73.0	3.9	72.9	20.3
benzene	17.5	9.3	22.9	0.3	21.5	2.0	20.6	19.0
n-heptane	10.8	5.2	17.4	0.1	9.7	1.6	12.6	32.3
toluene	31.5	9.5	54.1	4.0	48.9	3.9	44.8	24.9
1.3 + 1.4-xylene	38.2	5.3	17.2	2.1	10.9	0.3	22.1	58.6
1.1.1 trichloro-ethane	12.9	6.4	10.4	1.0	16.7	0.3	13.3	26.1

Table 16 - Test compound concentrations determined with GASBADGE samplers exposed at Berlin

Compound	HIA mean* µg/m³	HIA difference* µg/m³	WaBoLu mean* µg/m³	WaBoLu difference* µg/m³	JRC mean* µg/m³	JRC difference* µg/m³	Mean conc. GASBADGE µg/m³	relative SD [%]
n-hexane	68.0	41.2	96.9	14.2	95.5	15.0	86.8	23.7
benzene	19.2	8.1	27.0	4.1	20.0	0.2	21.7	21.3
n-heptane	14.2	6.2	20.1	3.0	11.7	1.3	15.3	29.2
toluene	42.9	21.4	62.7	8.3	46.2	0.9	50.6	23.6
1.3 + 1.4 xylene	39.9	11.3	18.6	3.1	10.3	0.6	22.9	61.7
1.1.1-trichloro-ethane	15.0	11.4	13.8	2.9	17.2	1.0	15.3	26.4

* of the values obtained with the two samplers analyzed in each laboratory

Table 17 - Reproducibility R* and mean ratios RA** of test compound concentrations determined with each couple of samplers

	OVM-3500				GASBADGE			
	R (%) ± SD		RA ± SD		R (%) ± SD		RA ± SD	
H I A	40.6	15.4	1.35	0.43	50.1	16.5	1.40	0.50
WaBoLu	8.0	6.3	1.08	0.07	16 1.9 a)	2.7 1.9a)	1.17	0.03
JRC	7.3	5.4	1.07	0.07	7.3	5.1	1.01	0.10

a) values obtained if the concentrations of one of the two samplers are divided by the mean ratio RA = 1.17

* calculated using eq. (4

** calculated using eq. (5

For technical reasons at the HIA the analysis of the samplers was delayed for several months. The high values of R and RA may therefore be a result of sample changes. Out of the other results, only the reproducibility obtained with the GASBADGE sampler at the WaBoLu exceeds 10%. This appears to be due to differences between the two samplers, since concentrations determined with one of the samplers are consistently higher by a factor of 1.17 than those determined with the other sampler. In fact, correcting the concentrations of one of the samplers by this factor, a R-value of only 1.9% results. This finding confirms the conclusion drawn from the Aarhus experiment that there may be significant differences of adsorption/desorption characteristcs between samplers of the same type which need further investigation.

Accuracy. Table 18 compares the mean concentrations measured with the OVM-3500 and the GASBADGE samplers and the overall mean of the measured concentration values with the expected concentrations. The latter values differ by less than 40%. This is in agreement with the result of the Aarhus experiment.

Yet no clearcut conclusion can be drawn as to the reasons of the deviations between measured and expected values. They cannot be explained by the errors of the analytical steps following extraction of the samplers which are significantly lower and range between 5 and 15%. A few indications may be derived from Tables 18 and 19. Values in Table 19 have been calculated using eq. (7 and introducing the expected concentration values for c.

Table 18 shows that for most compounds the measured values are

Table 18 - Comparison of measured and expected test compound concentrations

Compound	Measured mean concentrations $\mu g/m^3$				EXPECTED ± SD %		△EXPECTED - MEASURED IN % OF EXPECTED	b.p. [°C]
	OVM-3500	GASBADGE	OVERALL ± SD	%				
n-hexane	72.9	86.8	79.9	23	117.5	5.4	32	69
benzene	20.6	21.7	21.3	20	34.9	0.2	39	80
n-heptane	12.6	15.3	14.0	31	19.5	2.2	28	98
toluene	44.8	50.6	47.7	24	72.6	11.7	34	111
1.3 + 1.4 xylene	22.1 14.0*	22.9 14.4*	22.5 14.2*	57 29*	17.5	5.7	-29 19*	138-9
1.1.1-trichloro-ethane	13.3	15.3	14.3	26	13.1	11.9	- 9	74

* excluding values measured at Aarhus

Table 19 - Accuracy AC obtained with the two sampler types in the three participating laboratories

	OVM-3500 AC [%] ± SD	GASBADGE AC [%] ± SD	AC % of Laboratories
HIA	53 ± 37	50 ± 40	54 ± 38
WaBoLu	20 ± 12	11 ± 8	20 ± 18
JRC	37 ± 8	35 ± 9	36 ± 8
AC [%] of sampler type	37 ± 26	32 ± 28	

smaller than the expected ones. For n-hexane, benzene and toluene the difference exceeds the standard deviation of the overall mean of measured concentrations. Sample loss by re-evaporation from the samplers which could be considered as an explanation, should show some dependence on the boiling points of the test compounds which is not observed (see b.p. values included in Table 18).

On the other hand Table 19 suggests that the storage time of samplers (or their history?) may have an influence on the accuracy. In fact the AC value is smallest for the WaBoLu where analysis has been performed immediately after exposure and highest for the HIA, where analysis could be performed only several months after exposure. Table 19 does not indicate any significant difference between the two sampler types.

CONCLUSIONS

The described experiments aimed at a first rather rough evaluation of the applicability of passive samplers to the assessment of organic indoor pollution.

The most important finding is that there are apparent differences between samplers of the same type. It has not been possible to elucidate the reasons for these differences. Theoretically inhomogeneities of the exposure chamber atmosphere, or differences of the adsorption or desorption characteristics may play a role. This is an important point which deserves further attention since it affects significantly the reproducibility and the accuracy of the results.

Overall reproducibility and accuracy has been within about 40% but reproducibility was 15-20% or better if systematic differences between samplers were corrected for. This is an acceptable result in view of the fact that each of the participating laboratories had to manipulate samplers without being familiar with all types used.

A more detailed study on a larger number of samplers would be highly desirable. For this study a common analytical protocol should be established and an effort should be made to control the concentrations of test compounds in the test chamber using different independent methods.

REFERENCES

/1/ NIOSH: "Organic Solvents in Air, Analytical Method n.P. & CAM 127, 15/2 1977, DHEW (NIOSH) 77-156 A"

/2/ B. SEIFERT and H.J. ABRAHAM: "Use of Passive Samplers for the Determination of Gaseous Organic Substances in Indoor Air at Low Concentration Levels", Intern. J. Environm. Anal. Chem. 1983, 13, 237-253.

ANNEX I

3M
Organic Vapor Monitor
Sampling Guide
For
Organic Vapor Monitor #3500/3510
Organic Vapor Monitor
With Back-Up Section #3520

December, 1982

ANOTHER STEP TOWARDS BETTER OCCUPATIONAL HEALTH AND SAFETY
R35SG-A(1221)R2
Litho in U.S.A.

Occupational Health and Safety Products Division/3M
220-7W 3M Center
St. Paul, Minnesota 55144

Use of the Sampling Guide Tables:

The following table summarizes OSHA standards, 3M monitor sampling information and recommended sampling procedures for a variety of organic compounds for which the 3M Organic Vapor Monitors can be used to acccurately determine the environmental exposures. The table is not exhaustive and will be updated periodically. To obtain periodic updates, retum the registration card contained in every box of monitors to 3M Company.

A. OSHA Standards

The OSHA TWA-PEL's (Time Weighted Average) given as workshift time weighted averages are taken from the Federal Register as found in 29 CRF 1910.1000 as of 1 January 1977 and are summarized in the "NIOSH/OSHA Pocket Guide to Chemical Hazards." Also included in parentheses are the current ACGIH (American Conference of Governmental Industrial Hygienist) values in cases where they differ from OSHA TWA's. These values are subject to change and appropriate publications should be consulted for the most current information.

B. Monitor Samples Information

*** Sampling Rate**

All sampling rates have an accuracy of ± 5%. The (*) compounds in the Sampling Guide tables have been subjected to an extensive amount of laboratory work to verify the sampling rate. The sampling rates given for the remaining compounds in this table were determined from empirical relationships as outlines in a publication on Sampling Rate Validation. The sampling rates are tabulated as cubic centimeters/minute and micrograms/ppm-hour. The publication on Sampling Rate Validation Protocol can be obtained upon request from 3M Company.

The top section of the #3520 (containing the primary absorbent) has the same geometric dimension as the 3M Organic Vapor Monitor #3500. Therefore, the sampling rates are the same, and also have an accuracy of ±5%.

*** Capacity**

The capacity of the monitor for each individual compound is a function of molecular structure, vapor pressure, environmental conditions, etc. The capacity values are tabulated in Section II - Analysis Guide, and are used to determine the length of a recommended sampling period.

Because of the backup section, the effective sampling capacity of the Organic Vapor Monitor #3520 is four times greater than the values listed for the Organic Vapor Monitor #3500/3510.

When sampling environments containing contaminant mixtures on environments with high relative humidity, it is difficult to accurately define the diffusional sampling capacity. Therefore, under these conditions, the weight (Ws) collected by the secondary absorbent of the backup section can be compared with the weight (Wp) collected by the primary absorbent to determine sample validity. The ration Ws/Wp must be equal to or less than 0.50.

C. Length of Sampling Period

1. General

3500/3510

When sampling for organic contaminants, full workshift sampling periods are recommended as the most comprehensive measures of worker exposure. When sampling some organic contaminants, sampling periods shorter than a full workshift are required in order to sample within the recommended capacity of the monitor. Under these circumstances, sequential sampling with several monitors can be performed.

3520

For those compounds where the recommended length of the sampling period for the Organic Vapor Monitor 3500/3510 is less than a full workshift, the length of the sampling period can be increased by a factor of four when using the Organic Vapor Monitor #3520. Because of the increased effective capacity of the Organic Vapor Monitor #3520, sampling periods longer than a full workshift are possible. **The preferred recommendation is for full workshift sampling periods.**

2. **Effect on Humidity**

   Recommended sampling periods have been tabulated for concentration ranges from .1 to .5 times the PEL and from .5 to 3 times the PEL for relative humidities less than or greater than 70%. These recommended sampling periods should not be exceeded when using OVM #3500/3510.

3. **Minimum Sampling Time**

   To confirm quantitatively the presence and concentration of a contaminant in the atmosphere, most analysts must have a minimum of 10 micrograms for G.C. analysis. A sampling period of at least 15 minutes is recommended even when 10 micrograms of the contaminant could be collected in a shorter period. For a contaminant at a low concentration level, the sampling rate of micrograms/ppm-hr. should be used to verify a sampling period during which at least 10 micrograms of the contaminant would be collected.

D. Short Term Exposure Limit (STEL)

The ACGIH has recommended a short-term exposure limit (STEL) as a maximum concentration to which workers can be exposed for a period up to 15 minutes continuously. No more than four (4) such excursions per day are permitted, with at least 60 minutes between exposure periods, provided that the recommended ACGIH daily TLV-TWA also is not exceeded. The STEL values summarized in the following tables can be found in the "Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1980." The monitor is recommended for STEL sampling if, during the 15 minute sampling period, the monitor will collect a minimum of 10 micorgrams of the contaminant when sampling at the STEL concentrations.

E. Unsuitable Compounds

The OVM is not recommended for the compounds listed below because of adverse or inadequate interactions with the sorbent material. This list is representative of classes of compounds not suitable for use with the OVM.

Compounds not on this list or the Compound Guide should be handled by consultation with OH&SP Technical Service.

Compounds

Ammonia	Methane, Ethane, Propane
Carbon Monixide (1)	Methyl Alcohol (Methanol)
Ethylene Oxide (2)	Methyl Chloride
Formaldehyde (3)	Methyl, Dimethyl, Trimethyl Amines
Hydrogen Sulfide	Organic Solids
Isocyanates	Sulfur Dioxide

(1) Carbon Monixide can be monitored using 3M Monitor #3400
(2) Ethylene Oxide can be monitored using 3M Ethylene Oxide Monitor #3550/3551
(3) Formaldehyde can be monitored using 3M Formaldehyde Monitor #3750/3751

F. Compounds Printed in Bold Type

All compounds listed in **bold** type in the OVM Sampling Guide will be analyzed by 3M for the OVM #3510. †For more information contact your 3M Sales Representative or your local OH&SP Safety Products Distributor.

†Pre-paid analysis for up to three compounds.

The contaminant concentration can be calculated with the following information:

- **Sampling Information**
  Contaminant
  Length of Sampling Period (min.) t
- **Contaminant Information from Tables in Analysis Guide**
  Calculation Constant A or B
- **Analytical Results**
  Contaminant weight recovered W (Micrograms)
  Recovery Coefficient (r)

The time-weighted-average concentration in milligrams per cubic meter of the contaminant in the environment sampled can be calculated from the following expression:

$$C(mg/m^3) = \frac{W\ (micrograms)}{r \times t\ (minutes)} \times A$$

The time-weighted-average concentration in parts per million (ppm) of the contaminant can be calculated from the following expression:

$$C(ppm) = \frac{W\ (micrograms)}{r \times t\ (minutes)} \times B$$

The above expressions calculate the time-weighted-average concentrations at a sampling temperature of 25°C (298°K) and pressure of 760 mm. When sampling at other environmental conditions, the above expressions need to be corrected only for variations in temperature. The above expressions can be multiplied by the following temperatures correction factors (CF_T) for samples collected at temperatures other than 25°C (77°F).

Sampling Temperature (°C)	Temperature (°F)	Temperature Correction Factor (CF_T)
44	111	.97
37	99	.98
31	88	.99
25	77	1.00
19	66	1.01
13	55	1.02
7	45	1.03
2	36	1.04
− 3	27	1.05
− 8	18	1.06

From the above table, every 10-11° above or below 77°F requires a one percent correction to the calculated time-weighted-average concentration.

If the temperature correction is desired, the time weighted average concentration can be calculated by the following expression:

$$C(mg/m^3) = \frac{W\ (micrograms)}{r \times t\ (minutes)} \times A \times CF_T$$

$$C(ppm) = \frac{W\ (micrograms)}{r \times t\ (minutes)} \times B \times CF_T$$

Example Calculation

Contaminant	Benzene
Length of Sampling Period (t)	420 minutes
Temperature (T)	75°F
Calculation Constant A	28.2
or	
B	8.83
Contaminant Weight Recovered (W)	27.2 micrograms
Recovery Coefficient(r)	1.02

Using Calculation Constant A:

$$C(mg/m^3) = \frac{27.2}{(1.02)\ (420)} \times 28.2$$

$C = 1.79\ mg/m^3$

Using Calculation Constant B:

$$C\ (ppm) = \frac{27.2}{(1.02)\ (4.20)} \times 8.83$$

$C = .56\ ppm$

Sampling Guide

COMPOUND	RECOMMENDED SAMPLING PERIOD (Hrs.)				SHORT TERM EXPOSURE LIMIT (15 min.)		OSHA Standard TWA-PEL ( ) ACGIH TLV C-Ceiling (ppm)	SAMPLING RATE	
	RH < 70%		RH > 70%						
	.1-.5 PEL	.5-3 PEL	.1-.5 PEL	.5-3 PEL	STEL (ppm)	OVM Usage		(cc/min.)	Microgram / ppm/hr.
Acetone*	1	0.5	1	0.5	1250	Yes	1000	40.1	5 71
Acetonitrile*	8	2	6	1	60	Yes	40	48.2	4.85
Acrylonitrile	8	2	6	1	—		2	43.8	5.70
Allyl Alcohol	8	8	8	6	2	No	2	40.4	5.75
Allyl Chloride	8	8	8	6	2	No	1	35.1	6.63
n-Amyl Acetate*	8	8	8	4	150	Yes	100	26 0	7.36
s-Amyl Acetate	8	8	8	4	—		125	27.2	8 68
n-Amyl Alcohol*	8	8	8	4	—		(100)	31.4	6.78
i-Amyl Alcohol*	8	8	8	4	125	Yes	100	32.3	6.98
s-Amyl Alcohol	8	8	8	4	—		(100)	32.3	6.98
Benzene*	8	8	8	6	25	Yes	10	35.5	6.78
Benzyl Chloride	8	8	8	6	—		1	27.2	8.48
Bromoform	8	8	8	6	—		0.5	29.3	18.19
Butadiene	0.4	NR	0.4	NR	1250	Yes	1000	42.8	5.67
n-Butyl Acetate	8	7	6	3	200	Yes	150	31.6	9.00
s-Butyl Acetate	8	5	6	3	250	Yes	200	28 6	8 14
t-Butyl Acetate	8	4	6	3	250	Yes	200	29 4	8.37
Butyl Acrylate	8	8	8	6	—		— (10)	28.7	9 01
Butyl Alcohol*	8	8	8	4	—		100 (50)	34.3	5.55
s-Butyl Alcohol	8	6	6	3	—		150	34.8	6.32
t-Butyl Alcohol	8	7	6	3	150	Yes	100	35.2	6.39
Butyl Cellosolve* (2-Butoxyethanol)	8	8	8	6	150	Yes	50	28.2	8.15
Butyl Glycidyl Ether (BGE)	8	8	8	6	—		50	27.0	8 61
p-tert-Butyltoluene*	8	8	8	6	20	Yes	10	20 7	7.51
Camphor	8	8	8	6	3	No	2	21.4	7.11
Carbon Disulfide	8	2	6	1	—		20	42.8	7.88
Carbon Tetrachloride*	8	8	8	6	20	Yes	10	30.2	11.41
Cellosolve* (2-Ethoxyethanol)	8	5	8	3	150	Yes	200 (100)	32.4	7.14
Cellosolve Acetate* (2-Ethoxyethyl Acetate)	8	8	8	4	150	Yes	100	26.6	8.60
Chlorobenzene*	8	8	8	5	—		75	29.3	8.12
o-Chlorostyrene	8	8	8	6	75	Yes	— (50)	26.0	8.87
o-Chlorotoluene	8	8	8	6	75	Yes	— (50)	27.3	8 51
Chlorobromomethane*	8	1.5	6	1.5	250	Yes	200	34.4	10.89
Chloroform*	8	4	6	3	50	Yes	50 (10)	33.5	9.78
1-Chloro-1-nitropropane	8	8	8	8	—		20	30.4	9.25
Chloroprene (2-Chloro-1,3-butadiene)	8	8	6	4	—		25 (10)	32.2	7.03
Cumene*	8	8	8	6	75	Yes	50	24.5	8 82
Cyclohexane*	8	3	6	2	375	Yes	300	32.4	6.67
Cyclohexanol*	8	8	8	6	—		50	29 5	7.24
Cyclohexanone*	8	8	8	6	—		50	28.9	6.94
Cyclohexene*	8	3	6	2	—		300	32.3	6.49
Diacetone Alcohol*	8	8	8	6	75	Yes	50	28.2	7.15
o-Dichlorobenzene*	8	8	8	6	—		50	27 8	10.03
p-Dichlorobenzene*	8	8	8	6	110	Yes	75	27.8	10 03
1,1-Dichloroethane	8	1.5	4	1.5	250	Yes	100 (200)	33.2	8 07
1,2-Dichloroethylene*	1	0.2	1	0.2	250	Yes	200	35.2	8 38
1,1-Dichloro-1-nitroethane	8	8	8	6	10	Yes	10	28.5	10.07
Dichloroethyl Ether	8	8	8	6	10	Yes	15 (5)	26.1	9.16
Diisobutyl Ketone* (DIBK)	8	8	8	6	—		50	24.6	8.56

Sampling Guide

COMPOUND	RECOMMENDED SAMPLING PERIOD (Hrs.)				SHORT TERM EXPOSURE LIMIT (15 min.)		OSHA Standard TWA-PEL ( ) ACGIH TLV C-Ceiling (ppm)	SAMPLING RATE	
	RH < 70%		RH > 70%						
	.1-.5 PEL	.5-3 PEL	.1-.5 PEL	.5-3 PEL	STEL (ppm)	OVM Usage		(cc/min.)	Microgram / ppm/hr.
Dimethyl Formamide (DMF)	8	8	8	6	20	Yes	10	32.4	5.8
p-Dioxane	8	8	8	4	—		100 (50)	34.5	7.45
Dipropylene Glycol Methyl Ether	8	8	8	4	150	Yes	100	25.3	9.19
Enflurane (2-Chloro-1,1,2 trifluoroethyl difluoromethyl ether)	8	8	8	6	—		— (2)	28.3	12.81
Epichlorohydrin (1-Chloro-2,3-epoxy-propane)	8	8	8	6	5	No	5 (2)	29.6	6.76
Ethyl Acetate*	7	1	4	1	—		400	34.5	7.45
Ethyl Acrylate	8	8	6	4	—		25	32.2	7.90
Ethyl Alcohol	4	0.5	4	0.5	—		1000	51.2	5.78
Ethyl Benzene	8	8	8	4	125	Yes	100	27.3	7.10
Ethyl Bromide*	1	0.2	1	0.2	250	Yes	200	36.4	9.74
Ethyl Butyl Ketone (3-Heptanone)	8	8	8	6	75	Yes	50	28.0	7.83
Ethyl Ether	0.3	NR	0.3	NR	500	Yes	400	36.8	6.68
Ethyl Formate	3	0.5	3	0.5	150	Yes	100	38.8	7.04
Ethylene Chlorohydrin (2-Chloroethanol)	8	8	8	6	—		5	33.9	6.66
Ethylene Dibromide* (1,2-Dibromomethane)	8	8	8	6	—		20	29.6	13.66
Ethylene Dichloride* (1,2-Dichloroethane)	8	8	6	4	15	Yes	50 (10)	33.2	8.07
Furfural	8	8	8	8	15	Yes	5	34.3	8.08
Furfuryl Alcohol	8	8	8	6	10	Yes	50 (5)	32.6	6.98
Glycidol (2,3-Epoxy-1-propanol)	8	8	8	6	75	Yes	50	37.1	6.74
Halothane (2-Bromo-2-chloro-1,1,1 trifluoroethane)	8	8	6	4	—		— (2)	30.2	14.63
Heptane*	8	2	4	2	500	Yes	500 (400)	28.9	7.08
Hexachloroethane	8	8	8	8	3	Yes	1	26.7	15.53
Hexane*	8	1.5	4	1.5	125	Yes	500 (100)	32.0	6.74
s-Hexyl Acetate	8	8	8	4	—		50	28.1	9.93
Isoamyl Acetate	8	8	8	4	125	Yes	100	27.2	8.68
Isoamyl Alcohol*	8	8	8	4	125	Yes	100	32.3	6.98
Isobutyl Acetate*	8	8	8	4	187	Yes	150	31.0	8 82
Isobutyl Alcohol*	8	8	6	4	75	Yes	100 (50)	35.9	5 81
Isophorone*	8	8	8	6	—		25 (5)	21.7	7.34
Isopropyl Acetate	8	2	6	2	310	Yes	250	31.7	7.93
Isopropyl Alcohol	8	2	6	2	500	Yes	400 (250)	39.4	5.17
Isopropyl Ether	5	0.8	4	0.8	310	Yes	500 (250)	31.2	7.81
Isopropyl Glycidyl Ether	8	8	8	6	75	Yes	50	29.1	8.28
Mesityl Oxide*	8	8	8	6	—		25	31.2	7.49
Mesitylene* (Trimethyl Benzene)	8	8	8	6	35	Yes	25	26.3	7.73
Methyl Acetate*	3	0.5	3	0.5	250	Yes	200	37.9	6.72
Methyl Acrylate	8	7	6	3	—		10	35.8	7.56
Methylal (Dimethyoxymethane)	0.3	NR	0.3	NR	1250	Yes	1000	37.9	7.07
Methyl Amyl Ketone (2-Heptanone)	8	8	8	4	150	Yes	100	27.9	7.81
Methyl Bromide	4	0.5	3	0.5	—		20 (15)	46.5	10.84

Sampling Guide

COMPOUND	RECOMMENDED SAMPLING PERIOD (Hrs.)				SHORT TERM EXPOSURE LIMIT (15 min.)		OSHA Standard TWA-PEL ( ) ACGIH TLV C-Ceiling (ppm)	SAMPLING RATE	
	RH < 70%		RH > 70%						
	.1-.5 PEL	.5-3 PEL	.1-.5 PEL	.5-3 PEL	STEL (ppm)	OVM Usage		(cc/min.)	Microgram / ppm/hr.
Methyl Butyl Ketone* (2-Hexanone)	8	8	8	4	50	Yes	100	29.7	7.29
Methyl Isobutyl Ketone* (Hexanone)	8	8	8	4	125	Yes	100	30.0	7.35
Methyl Cellosolve* (2-Methoxyethanol)	8	8	8	6	35	Yes	25	36.3	6.76
Methyl Cellosolve Acetate* (Ethylene Glycol Methyl Ether Acetate)	8	8	8	6	35	Yes	25	29.0	8.38
Methyl Chloroform*	6	1	4	1	450	Yes	350	30.9	10.09
Methyl Cyclohexane*	8	2.5	6	2	500	Yes	500	28.9	6.94
Methyl Cyclohexanol	8	8	8	4	75	Yes	100 (50)	28.8	8.06
Methyl Ethyl Ketone* (2-Butanone)	8	3	6	2	300	Yes	200	36.3	6.41
Methyl Formate	0.7	NR	0.7	NR	150	Yes	100	45.0	6.33
5-Methyl-3-heptanone (Ethyl Amyl Ketone)	8	8	8	6	—		25	26.4	7.39
Methyl Iodide	6	1	4	1	10	Yes	5	36.7	12.79
Myethyl Isobutyl Carbinol (Methyl Amyl Alcohol)	8	8	8	6	40	Yes	25	29.2	6.51
Methyl Isoamyl Ketone	8	8	8	4	150	Yes	100	28.0	7.83
Methyl Methacrylate	8	8	8	4	125	Yes	100	31.8	7.80
Alpha Methyl Styrene*	8	8	8	4	—		100	25.0	7.24
Methylene Chloride* (Dichloromethane)	1	0.2	1	0.2	250	Yes	500 (200)	37.9	7.91
Naphtha (VM&P)*	8	2	6	2	400	Yes	300	33.2	8.15
Naphthalene	8	8	8	6	15	Yes	10	24.6	6.88
Nonane*	8	5	6	3	250	Yes	— (200)	24.6	7.71
Octane*	8	3	8	2	375	Yes	500	26.6	7.43
Pentane*	2.5	0.4	2.5	0.4	750	Yes	1000 (600)	35.3	5.56
2-Pentanone* (Methyl Propyl Ketone)	8	5	6	3	250	Yes	200	33.0	6.95
Perchloroethylene (Tetrachloroethylene)	8	7	6	3	150	Yes	100	28.3	11.53
Phenyl Ether	8	8	8	6	2	No	1	24.1	10.05
Phenyl Glycidyl Ether	8	8	8	6	15	Yes	10	20.8	7.71
n-Propyl Acetate*	8	4	8	3	250	Yes	200	30.1	7.53
n-Propyl Alcohol*	8	8	6	4	250	Yes	200	39.7	5.21
Propylene Dichloride* (1,2-Dichloropropane)	8	8	6	4	110	Yes	75	30.6	8.49
Propylene Glycol Monomethyl Ether	8	8	8	4	150	Yes	— (100)	32.4	6.09
n-Propyl Nitrate	8	8	8	4	40	Yes	25	33.3	7.27
Stoddard Solvent	8	4	6	3	125	Yes	500 (100)	24.3	8.59
Styrene*	8	8	8	4	125	Yes	100	26.8	6.83
1,1,2,2-Tetrachloroethane	8	8	8	6	10	Yes	5	28.4	11.71
1,1,1,2-Tetrachloro-2,2-difluoroethane	5	0.75	4	0.75	625	Yes	500	29.7	14.87
1,1,2,2-Tetrachloro-1,2-difluoroethane	5	0.75	4	0.75	625	Yes	500	28.2	14.12
Tetrahydrofuran	8	2	4	2	250	Yes	200	37.2	6.57
Toluene*	8	6	6	3	150	Yes	200	31.4	7.08
1,1,2-Trichloroethane*	8	8	6	6	20	Yes	10	29.7	9.69
Trichloroethylene*	8	8	8	6	150	Yes	100 (50)	31.1	10.00
1,1,2-Trichloro-1,2,2-trifluoroethane	0.5	NR	0.5	NR	1250	Yes	1000	31.4	14.41
1,2,3-Trichloropropane	8	8	8	6	75	Yes	50	27.4	9.88
Vinyl Acetate	8	8	6	4	20	Yes	— (10)	35.8	7.56
Vinyl Bromide	2	2	2	2	—		(5)	41.0	10.77
Vinyl Chloride*	2	2	2	1.5	—		1 (5)	40.9	8.22
Vinylidene Chloride	2	2	2	2	20	Yes	(10)	38.6	9.19
Vinyl Toluene	8	8	6	4	150	Yes	100	26 8	7.75
Xylene*	8	8	6	4	150	Yes	100	27.3	7.09

ANNEX II

G A S B A D G E

ORGANIC VAPOR DOSIMETER

- Use and Analysis Instructions -

September 1980 Edition

Organic Vapor Dosimeter

Use and Analysis Instructions

September 1980 Edition

National Mine Service Company

Safety Systems and Products Division

Acknowledgements

Much of the information contained in these instructions has been abstracted or reproduced from NIOSH Method No. P&CAM 127, ORGANIC SOLVENTS IN AIR, contained in the NIOSH Manual of Analytical Methods, DHEW (NIOSH) Publication No. 77-157A, B&C and other similar methods developed by NIOSH.

The procedures recommended in this manual will yield analytical results comparable with the results obtained in the analysis of charcoal tubes using these analytical methods.

We wish to acknowledge the significant efforts of NIOSH in the development of Method P&CAM 127. The similarities of National Mine Service Co. recommended analytical instructions to the NIOSH method are not meant to imply endorsement or approval by NIOSH of the GASBADGE Organic Vapor Dosimeter. There are no devices approved by NIOSH for obtaining eight-hour time-weighted-average exposures for organic vapors.

Table of Contents

1. Introduction

The techniques you currently use to analyze charcoal tubes on a gas chromatograph (GC) will apply to the analysis of the GASBADGE organic vapor collection element. After you review the instructions contained in this booklet, you may continue to use your present analysis method after modifying it appropriately.

1.1 Principles of the Method. The GASBADGE Organic Vapor Dosimeter uses principles of diffusion and chemical adsorption to collect organic vapors or gases in the industrial environment.[1,2] Subsequent analysis of the collected vapors is done by gas chromatography, utilizing solvent desorption techniques.[3] The practical application of these principles and techniques makes the GASBADGE Organic Vapor Dosimeter an excellent tool for monitoring exposures of personnel to organic vapors and gases.

1.2 Conducting a Monitoring Program. A monitoring program can involve several individuals often separated by large distances and varying levels of technical expertise. It requires knowledge of employee work routines, and the areas in which they can be exposed to potentially hazardous materials.[4] Obtaining accurate employee exposure information requires adequate training of field and laboratory personnel. This manual will provide the necessary training of such personnel to assure accurate results in the following areas.

1.2.1 Preparing the Dosimeter — Loading the dosimeter; labeling and records-keeping.

1.2.2 Field Sampling — Putting a loaded GASBADGE Organic Vapor Dosimeter on the employee; making sure a blank is properly taken; noting any conditions that could affect the collection of vapors and gases.

1.2.3 Treatment of Exposed Samples — Removing the collection element from the dosimeter; putting the element into a collection vial; labeling and records-keeping; transporting to the analytical laboratory.

1.2.4 Sample Analysis — Preparing a standard curve; desorption efficiencies; sample analysis.

1.2.5 Preparing a Report — Calculating results: compiling employee exposure information; preparing the report.

1.3 Range and Sensitivity. The useful range of the dosimeter is 0.20-200 ppm for an 8-hour exposure. This range will vary, depending upon the substances being monitored, the sensitivity of the GC apparatus, and the length of the exposure time. In general, the minimum sensitivity is determined by the sensitivity of the gas chromatograph to the material being analyzed. The maximum loading capacity for GASBADGE collection elements is 10 mg. For additional information, see Section 1.5.

1.4 Precision and Accuracy. The mean relative standard deviation of the analytical method and sample collection using the GASBADGE Organic Vapor Dosimeter is 4.8% for benzene. The dosimeter meets OSHA accuracy requirements for benzene monitoring of ± 25% at a 95% confidence level.

1.5 Advantages. The dosimeter is small, portable, and involves no liquids. Interferences are minimal, and one can eliminate most of those that do occur by altering chromatographic conditions. The dosimeter collection element is analyzed by a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected of being present in the same sample.

It is difficult to overload the GASBADGE dosimeter at concentrations of interest, since it can readily sample 150-200 ppm of most organic vapors for 8 hours. Additionally, the amount of activated carbon in the GASBADGE dosimeter allows collection of at least 15 mg of organic vapors. If a total of more than 10 mg of organic solvents is collected on the activated carbon collection element, one should suspect overloading of the dosimeter.

If the exposure area is suspected of having a high concentration of organic solvent vapors, more than one dosimeter can be used to obtain consecutive samples for shorter time periods. Using two dosimeters to collect two consecutive samples of 4 hours each doubles the range, etc.

1.6 Interferences. Technical literature indicates that high humidity alters adsorption for various organic solvents.

When two or more solvents are suspected of being present in the air, such information, including their probable identities, should be transmitted with the sample, since one may displace another from the activated carbon.

It must be emphasized that any compound which has the same retention time as the specified compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single GC column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason, it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

---

2. Monitoring Employee Exposure

2.1 Preparing the Dosimeter.

Figure 1

Figure 2

2.1.1 The GASBADGE Organic Vapor Dosimeter package (Figure 1) contains:

a. 5 Dosimeters (unloaded)
b. 10 Collection Elements
c. 10 Draft Shields
d. 10 Sample Vials and Mailer
e. 10 Monitoring Information Labels
f. 1 Tamper
g. 1 Pair Forceps

2.1.2 The GASBADGE Organic Vapor Dosimeter (Figure 2) has the following components when loaded:

a. Sliding Cover
b. Dosimeter Front with opening to allow diffusion of gases or vapors into dosimeter
c. Protective Screen
d. Draft Shield
e. Open Grid to define diffusion geometry
f. Replaceable Collection Element
g. Dosimeter Back with spring clip

Figure 3

Figure 4

2.1.3 To prepare dosimeter for monitoring:

a. Slide cover completely off.
b. Place the index finger of one hand on the opening of the dosimeter front. Hold sides of dosimeter with other hand (Figure 3).
c. Press down with index finger to separate components.

2.1.4 To load the dosimeter:

a. Place the front face down.
b. Insert protective screen in section of dosimeter front with opening.
c. Place draft shield on top of protective screen (Figure 4).
d. Place back with clip down on table.
e. Remove collection element from sealed package.

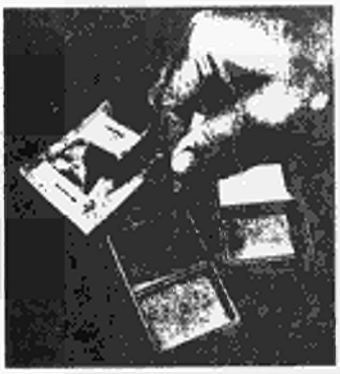

Figure 5

Figure 6

f. Place collection element in top section of dosimeter back (Figure 5). **For at least one dosimeter of the group, place an additional collection element in the bottom section as a blank.** (See Section 2.3.2e.)
g. Place grid into back of dosimeter. Make sure the edge with the lip touches the collection element (Figure 6).
h. Press front and back halves of the dosimeter case together (Figure 7).
i. Slide cover all the way to the top of the dosimeter (Figure 8).
j. Put an exposure information label on the back of the sliding cover of each dosimeter.
k. The dosimeter is now loaded and ready for use.
l. Prepare an information sheet, listing employees to be monitored. It should contain the following data:
    1. I.D. number
    2. Lot number of collection elements

3. Date of exposure
4. Name of employee monitored
5. Social Security number
6. Vapors monitored
7. Other pertinent data, e.g., job description

Figure 7

Figure 8

2.2 Monitoring Employee Exposure.

2.2.1 The GASBADGE dosimeter generally will be used for time-weighted average (TWA) exposures of several hours duration. "Grab" samples may be collected for short sample periods, e.g., 15 minutes, if vapor concentration is high enough to provide sufficient material for analysis.

2.2.2 To begin monitoring with the GASBADGE dosimeter:

a. Write required information on label on back of each dosimeter.
b. Slide cover down to begin exposure.
c. Clip dosimeter near employee's breathing zone (see inside front cover).
d. Instruct the employee to report any extreme conditions that could affect the monitoring, such as high temperature, high humidity, or splashes on the face of the dosimeter.
e. Allow employee to resume his or her normal work schedule.
f. Exposure time generally is 8 hours, although longer or shorter times may be used.
g. Remove dosimeter at the end of exposure period.
h. Slide cover up to end exposure.

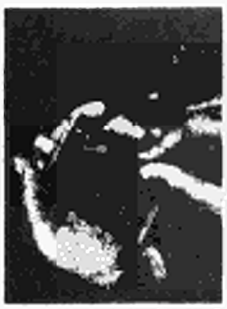

Figure 9

Figure 10

Figure 11

2.3 Treatment of Exposed Samples.

2.3.1 To remove collection element from the dosimeter:

a. Open the dosimeter (Figure 3) in an area free of organic vapors.
b. Remove the grid.
c. Using sharp-pointed forceps, roll up the collection element (Figure 9).
d. Twist element into sample vial (Figure 10).
e. Use the tamper provided in the collection element kit or forceps to gently push the collection element so that it occupies the bottom half of the vial (Figure 11).
f. Close the vial tightly.
g. Remove exposure information label from back of dosimeter and attach it to the sample vial.

2.3.2 To ship samples to the laboratory:

a. Place vials into the GASBADGE® Analysis Services mailer.
b. Fill in information required on the mailer.
c. Be sure to include the complete chemical name, **no abbreviations or trade names.** For example, if trichloroethane is abbreviated as "TCE," it could be misinterpreted as trichloroethylene or tetrachloroethane.
d. Immediately mail samples to National Mine Service Co. (or send to your company laboratory) for analysis.
e. Treat "blank" element in same fashion as exposed elements. Label vial "blank" and send it with the exposed samples for analysis. See Section 2.1.4f.)

3. Analytical Procedures

3.1 Introduction. The analytical method used is based on NIOSH Method No. P&CAM 127, ORGANIC SOLVENTS IN AIR.[3] In general, the only significant difference in the analysis of GASBADGE organic vapor collection elements from the analysis of charcoal tubes is that the sample size usually is smaller. This is due to:

a. less vapor/gas collected by diffusion, and
b. a larger amount of carbon disulfide (CS_2) is added to the collection elements in order to completely desorb the sample.

With a well-calibrated gas chromatograph, accurate determination of μg quantities of contaminant, e.g., benzene, is routinely possible.

Calculation of time-weighted-average concentrations in parts per million requires use of various standards, desorption studies, and quality control checks in addition to analysis of the samples. Standards are used to determine the concentrations of the samples by comparison with known concentrations. Since not all of the contaminant adsorbed on the charcoal will be eluted, desorption efficiencies must be determined at different concentrations. Periodic checking of the response of the gas chromatograph and other laboratory techniques requires that an ongoing quality assurance program be a part of the analysis.

3.2 Materials Required.

3.2.1 Equipment

a. Gas chromatograph equipped with flame ionization detector.
b. Any column which can provide the desired separation.
c. A mechanical or electronic integrator or a recorder and some method for determining peak area.
d. Septum-covered glass vials, A 3.7 ml screw-cap vial with a teflon-rubber disc and an open-top screw cap is recommended.
e. Hamilton syringes. 10 μl, or convenient sizes for making dilutions.
f. Pipets. 2.0 ml class A delivery pipets; pipets graduated in

0.1 ml increments; or appropriate repipets.

g. Volumetric flasks. 10 ml or convenient sizes for standards.
h. Laboratory hood.
i. Laboratory shaker.

3.2.2 Reagents

a. Spectroquality carbon disulfide, or other eluent as required.

WARNING

Acute carbon disulfide exposure can cause respiratory failure, and chronic exposure can cause severe psychological disorder[6].

b. Bulk sample of the compound under study.
c. Nitrogen, ultra pure — 99.995% or better (or other purified carrier gas)
d. Prepurified hydrogen — 99.995% or better.
e. Filtered compressed air.

3.2.3 Typical GC Conditions[7]

a. GC column: 10% FFAP on chromosorb W, AW-DMCS, 80/100 MESH, 20 ft × 1/8 in.
b. 30-50 cc/min. nitrogen carrier gas flow
c. 65 cc/min. hydrogen gas flow to detector
d. 500 cc/min. air flow to detector
e. 200°C injector temperature
f. Isothermal oven or appropriate temperature program. Other columns and settings would be appropriate if they accomplish the desired separation of the contaminant materials analyzed.

WARNING

Carbon disulfide is extremely flammable. GC injector temperatures and column connections should be carefully monitored. Auto ignition temperature is 100°C.[6]

3.2.4 Cleaning of Equipment

All glassware used for laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

3.3 Analytical Methods.

3.3.1 Desorption of Samples

Carbon disulfide is a suitable eluting solvent for most organics. Other eluting solvents may be used if they do not interfere with the GC analysis. The eluent is added to the vial containing the activated carbon collection element. It has been determined that a volume of 3.0ml, rather than 2.0ml of carbon disulfide or other eluent generally yields higher and more consistent desorption of collected samples. In addition, a 3.0ml solvent volume makes it easier to remove an aliquot of the desorbed sample for transfer to an auto-sampler vial. A 3.0ml desorption volume is not recommended if it would lower the concentration of analyte below the sensitivity of the gas chromatograph for the materials being analyzed. (Note: standards are prepared using the same volume of eluent as the samples). This step should be carried out in a hood due to the high toxicity of CS_2. For added protection and convenience, a septum cap is provided with each vial. The samples should be gently mixed at frequent intervals over a desorption time of 30 minutes. Use of a laboratory shaker is recommended. Care should be taken not to splash CS_2 on the inside of the septa as this could cause loss of CS_2.

3.3.2 Injection

The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10μl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2μl to separate the solvent flush from the sample with an air bubble that is used as a marker. The needle is then immersed in the sample, and a 5μl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle Duplicate injections of each sample and standard

should be made. No more than a 3% difference in area is to be expected. The analyte can also be transferred to the smaller vials of an auto sampler. Automated injections would then provide standardized injection technique[9].

3.3.3 Measurement of Area

The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve. (see Section 3.4)

3.4 Preparing a Standard Curve. It is convenient to express concentration of standards in terms of µg/2.0ml eluting solvent because samples are desorbed in this amount of eluent. A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by the plotting of concentration in µg/2.0ml versus peak area.

The weight, in µg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on µg/2.0ml eluting volume and the volume of sample injected is identical with the volume of the standards injected.

A rule of thumb for determining the range of interest for standards is to make solutions at 0.5, 1.0 and 2.0 × the maximum permissible exposure value. To calculate the amount of pure compound to add to 2.0ml CS_2 to correspond to this value, see Section 4.1.

To prepare standards at low concentrations, it may be necessary to add the analyte to a suitable solvent to obtain measurable quantities of the substance to be quantitatively added to the carbon disulfide.

Standards should be run in duplicate. The corresponding pairs should be averaged and plotted. The use of a regression analysis is helpful in determining the slope and intercept.

The standard curve should exhibit linearity over the range of interest. To calculate concentration (µg) from the standard curve (since it is of the form $y = mx + b$)

$$\mu g = \frac{\text{Area units} - \text{intercept}}{\text{slope}}$$

For detailed calculation procedures see Section 4.1.

3.5 Desorption Efficiencies. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of carbon to another. Thus, one must determine, at least once, the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of carbon is used. Since the desorption efficiency may not be constant over all concentrations, desorption efficiencies must be done at several concentrations. The concentrations are then plotted against the desorption efficiencies. The correct desorption efficiency for the concentration sampled can be read off the graph. It is advisable to determine desorption efficiencies using the same concentrations as the standards. Desorption efficiencies should be run in duplicate at the levels of interest.

To determine desorption efficiencies, place one activated carbon collection element in each of eight glass vials and inject known amounts of the analyte at three different concentrations directly into six of the vials. The remaining two collection elements in the glass vials which have not been injected with analyte serve as the blank. For low TWA levels it may be necessary to add the analyte to a suitable solvent to obtain measurable injection quantities of the substance of interest.

Cap the vials tightly and allow them to sit overnight. Then desorb and analyze the elements in the same manner previously described in Section 3.3.

Prepare three standards by injecting the same volume of compound in 2.0 ml of CS_2 or other eluting solvents with the same syringe used in the preparation of the samples. Analyze these with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the

blank divided by the average peak area of the standards, or:

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

For detailed calculation procedures, see Section 4.2.

3.6 Obtaining an Accurate Analysis. Samples should be desorbed and run with the standards and desorption efficiency samples. Uniform handling of the standards, desorption vials, and samples is necessary for accurate results. The midpoint of the standard curve should be run periodically during the analysis to assure machine and operator uniformity.

A sample blank should be run with each group of exposed samples. A CS_2 blank and a desorption efficiency blank should be run as often as required. The sample blank should be an element which was handled identically with the exposed samples, except that it was not intentionally exposed to the contaminant. The blank should have the same lot number, have traveled the same route, been stored, desorbed, and analyzed in the same way as were the exposed samples. The blank value in concentration units should be subtracted from each sample analyzed.

3.7 Quality Control. For a complete discussion of quality control in the industrial hygiene laboratory, see AIHA and NIOSH publications [8,9]

4. Calculations

4.1 Standard Curve. Standards of one-half, one and two times the TWA concentration, analyzed in duplicate, are recommended. To calculate the amount of pure compound to add to 2.0ml CS_2 to correspond to a TWA concentration for 8 hours, use the following formula:

$$\mu g = \text{TWA} \times mw \times D \times \frac{t}{3360} \qquad (1)$$

where:

TWA = maximum ppm concentration allowed for 8-hour exposure

mw = molecular weight of organic solvent
D = diffusion coefficient of organic solvent (see Appendix A or References 12 or 13)
t = 28,800 seconds for an 8-hour exposure (Note: time must be expressed in seconds.)
3360 = constant derived from molar volume considerations, temperature and pressure corrections, and dosimeter dimensions. Assumes temperature of 25°C, pressure of 760mmHg, both of which can be adjusted to reflect actual sampling conditions. Constant of 3360 is derived as follows:

$$22.400 cm^3/mole \times \frac{T°K}{273°K} \times \frac{760 mmHg}{P mmHg} \times \frac{1.31 cm}{9.54 cm^2}$$

where:

T = 298°K (25°C)
P = 760mmHg (1 atm)
1.31 cm = diffusion path length
$9.54 cm^2$ = cross-sectional diffusion area

For different exposure levels (e.g. 0.5 or 2.0 x TWA) or times adjust the relevant factors.

To convert the µg calculated into µl of organic solvent to be injected into the vial, use the following equation:

$$\mu l = \frac{\mu g}{\rho \times 1000} \qquad (2)$$

µg = value calculated from first equation
ρ = density of organic solvent in g/cc. generally at 25°C
(See References 12 or 13)
1000 = conversion factor for ρ to µg/µl

To determine the standard curve:

a. Determine the areas of the standards by GC analysis (see Section 3.4).
b. Average duplicate determinations of peak area of standards.
c. Plot average peak area vs. µg in standard.
d. Determine the slope and intercept of the standard curve — use a regression analysis.

e. To convert peak area of each exposed sample to μg using the following equation:

$$\mu g = \frac{\text{Peak Area} - \text{Intercept}}{\text{Slope}} \quad (3)$$

4.2 Desorption Efficiencies. To determine the number of μg adsorbed by the collection element under given exposure conditions and the amount of solvent (in μl) to be injected into the collection element, use equations 1 and 2 Section 4.1.

Since the maximum loading of the GASBADGE collection element is 10 mg of organic solvent, the μg calculated by equation should not exceed 10,000 μg. If the value calculated by the above equation exceeds 10,000 μg, use μg = 10,000 in the equation to convert μg to μl of organic solvent to be injected into the vial.

To determine the desorption efficiencies, average the duplicate determination of the peak areas for the desorption efficiency samples, blanks, and standards, respectively.

Calculate the desorption efficiency using the following equation:

$$\text{Desorption Efficiency} = \frac{\text{Area Sample} - \text{Area Blank}}{\text{Area Standard}} \quad (4)$$

4.3 Calculating Maximum ppm for an 8-Hour Exposure. The maximum ppm that the activated carbon collection element can monitor with confidence for a particular organic contaminant can be calculated using the following formula:

$$\text{ppm} = \frac{10{,}000\ \mu g \times 3360}{28{,}800\ \text{sec} \times \text{mw} \times D} \quad (5$$

where:

mw = molecular weight of organic solvent
D = diffusion coefficient of organic solvent
3360 = constant (defined in Section 4.1)
28,800 = t in seconds (8 hours)

Higher concentrations can be monitored by shortening the exposure time.

4.4 Determining Diffusion Coefficients. Diffusion coefficients are most accurately determined by actual measurement

under controlled laboratory conditions. The diffusion coefficients contained in Appendixes A and B were obtained by actual measurement and were compiled by Nelson[10], and reproduced by permission of the publisher.

If diffusion coefficients are not available, they can be calculated using Gilliland's approximation[11]. It should be emphasized that there can be significant variations (± 10% or more) between experimentally determined diffusion values and calculated diffusion values. Consequently, exposure concentrations determined using calculated diffusion coefficients should be considered estimated exposure concentrations rather than accurate values. For example, the calculated value for Benzene is 12.5% lower than the actual measured diffusion coefficient. For additional information on this method, refer to the above references or contact National Mine Service Co.

4.5 Calculating TWA (ppm) Exposure Values. The concentration of organic contaminant in air sampled for time is:

$$ppm = \text{corrected}\,\mu g \times \frac{1}{mw} \times 3360 \times \frac{1}{Dt\epsilon} \qquad (6)$$

where:

corrected μg = μg exposed sample − μg sample blank
mw = molecular weight of organic solvent
D = diffusion coefficient of organic solvent in air at 25°C in cm^2/sec.
t = time exposed (in seconds)
ε = desorption efficiency
3360 = constant (defined in Section 4.1)

5. Information Required by OSHA as a Record of Employee Exposure Measurements

In its Standard of February 10, 1978, on Occupational Exposure to Benzene, OSHA sets forth specific requirements for employer records of employee exposure measurements[14]. The record must include:

a) The dates, number, duration, and results of each of the

samples taken, including a description of the procedure used to determine representative employee exposures;

b) A description of the sampling and analytical methods used;

c) Type of respiratory protective devices worn, if any; and

d) Name, social security number, and job classification of the employee monitored and all other employees whose exposure the measurement is intended to represent.

Employers shall maintain this record for at least 40 years or the duration of the employment plus 20 years whichever is longer.

Similar record keeping requirements are advisable when monitoring other gases and vapors.

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11) Gilliland, E.R., Ind Eng. Chem., 26,681 (1934)
12) "The Merck Index", 9th Edition, Merck & Co., Inc., Rahway, NJ (1977)
13) The Handbook of Chemistry and Physics, 54th Edition, CRC Press, Cleveland, OH (1973).
14) Federal Register, February 10, 1978, Part II, page 5966

Appendix A

Physical and Chemical Values for Various Organic Solvents

Compound	TWA	MW	Dosimeter Sampling Constant	Density, ρ^{20}_4
Benzene	10	78.1	0 0816	0 87865
Heptane	400	100 2	0.0626	0.68376
n-Hexane	100	86.2	0.0692	0 6603
Monochlorobenzene	75	112 6	0 0686	1 1058
Pentane	600	72 2	0 0733	0.6262
Styrene	100	104.1	0.0691	0 9060
Tetrachloroethylene (Perchloroethylene)	100	165 9	0 0638	1 6227
Toluene	100	92.1	0 0715	0 8669
1,1,1 Trichloroethane (Methyl Chloroform)	350	133.4	0.0665	1 3390
Trichloroethylene	100	131 4	0.0698	1 4642
Xylene	100	106 2	0 0642	o - 0 8802 m - 0 8642 p - 0.8611

[1]Handbook of Chemistry and Physics, CRC Press 51st Edition (1971)

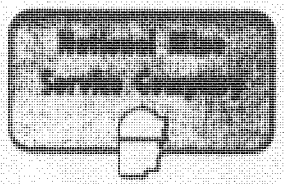
Appendix B

Diffusion Coefficients at 25°C and 760 mm Hg in Air*

Compound	Formula	Diffusion coefficient (cm^2/sec)
Acetone	$(CH_3)_2CO$	0.1049
Acrylonitrile	CH_2CHCN	0.1059
Allyl alcohol	CH_2CHCH_2OH	0.1021
Allyl Chloride	CH_2CHCH_2Cl	0.0975
Amyl acetate	$CH_3COO(CH_2)_4CH_3$	0.0610
Benzene	C_6H_6	0.0932
Benzyl chloride	$C_6H_5CH_2Cl$	0.0713
Bromoform	$CHBr_3$	0.0767
Butyl acetate	$CH_3COO(CH_2)_3CH_3$	0.0672
iso-Butyl acetate	$CH_3COOCH_2CH(CH_3)_2$	0.0690
iso-Butyl alcohol	$(CH_3)_2CHCH_2OH$	0.0880
Butyl alcohol	$CH_3(CH_2)_2CH_2OH$	0.0861
sec-Butyl alcohol	$CH_3CH_2CH(OH)CH_3$	0.0891
tert-Butyl alcohol	$(CH_3)_3COH$	0.0873
Carbon disulfide	CS_2	0.1045
Carbon tetrachloride	CCl_4	0.0828
Chlorobenzene	C_6H_5Cl	0.0747
Chloroform	$CHCl_3$	0.0888
Diacetone alcohol	$(CH_3)_2C(OH)CH_2COCH_3$	0.0647
1,2-Dibromoethane	CH_2BrCH_2Br	0.0826
Dibutyl phthalate	$C_6H_4[COO(CH_2)_3CH_3]_2$	0.0421
1,1-Dichloroethane	$CHCl_2CH_3$	0.0919
1,2-Dichloroethane	CH_2ClCh_2Cl	0.0907
sym-Dichloroethyl ether	$(ClCH_2CH_2)_2O$	0.0694
Dichloromethane	CH_2Cl_2	0.1037
Dioxane	$-O(CH_2)_2O(CH_2)_2-$	0.0922
Ethyl acetate	$CH_3COOC_2H_5$	0.0861
Ethyl alcohol	C_2H_5OH	0.1181
Ethyl benzene	$C_6H_5CH_2CH_3$	0.0755
Ethyl bromide	CH_3CH_2Br	0.0989
Ethylene chlorohydrin	CH_2C1CH_2OH	0.0964

Ethyl ether	$(C_2H_5)_2O$	0.0918
n-Hexane	$CH_3(CH_2)_4CH_3$	0.0732
Mesityl oxide	$(CH_3)_2CCHCOCH_3$	0.0760
Methyl acetate	CH_3COOCH_3	0.0978
Methyl ethyl ketone	$CH_3COC_2H_5$	0.0903
Methyl Formate	$HCOOCH_3$	0.1090
Octane	$CH_3(CH_2)_6CH_3$	0.0616
Pentane	$CH_3(CH_2)_3CH_3$	0.0842
iso-Propyl acetate	$CH_3COOCH(CH_3)_2$	0.0770
Propyl acetate	$CH_3COOCH_2CH_2CH_3$	0.0768
iso-Propyl alcohol	$(CH_3)_2CHOH$	0.1013
Propyl alcohol	$CH_3CH_2CH_2OH$	0.0993
iso-Propylbenzene (cumene)	$C_6H_5CH(CH_3)_2$	0.0677
iso-Propyl ether	$[(CH_3)_2CH]_2O$	0.0683
Styrene	$C_6H_5CHCH_2$	0.0701
1,1,2,2-Tetrachlorethane	CCl_2HCCl_2H	0.0722
Tetrachlorethylene	Cl_2CCCl_2	0.0797
Toluene	$C_6H_5CH_3$	0.0849
1,1,1-Trichlorethane	CCl_3CH_3	0.0794
1,1,2-Trichlorethane	CCl_2HCClH_2	0.0792
Trichlorethylene	$ClHCCl_2$	0.0875
m-Xylene	$C_6H_4(CH_3)_2$	0.0670
O-Xylene	$C_6H_4(CH_3)_2$	0.0727
p-Xylene	$C_6H_4(CH_3)_2$	0.0670

**Reproduced with permission of the publisher from "Controlled Test Atmospheres", Appendix F, G O Nelson Ann Arbor Science Publishers, Inc., Ann Arbor, MI 48106, 1972, pages 212-216.*



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